

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-389

Anonymous Referee #1

Referee comment on "Formaldehyde evolution in U.S. wildfire plumes during FIREX-AQ"
by Jin Liao et al., Atmos. Chem. Phys. Discuss.,
<https://doi.org/10.5194/acp-2021-389-RC1>, 2021

This manuscript analyzes formaldehyde data from select FIREX flights to better understand its production and loss and the drivers of secondary HCHO production. Overall, I found the science hard to follow as limited detail were given for the analyses. The descriptions and explanations need to be expanded to elevate the contribution and scientific the impact of the paper.

Specific Comments:

Line 192: How consistent was the background HCHO concentration? Was a single value appropriate to use as a cutoff?

Line 210: cited the paper! Coggon, Matthew M., Christopher Y. Lim, Abigail R. Koss, Kanako Sekimoto, Bin Yuan, Jessica B. Gilman, David H. Hagan, et al. "OH Chemistry of Non-Methane Organic Gases (NMOGs) Emitted from Laboratory and Ambient Biomass Burning Smoke: Evaluating the Influence of Furans and Oxygenated Aromatics on Ozone and Secondary NMOG Formation." *Atmospheric Chemistry and Physics* 19, no. 23 (December 10, 2019): 14875–99. <https://doi.org/10.5194/acp-19-14875-2019>.

Line 222: Which did you use or did the combination of the two help constrain the uncertainty? The slopes are different for each compound – that is due to the different k values of OH and O₃ for the 2 compounds? The use of these two compounds should be more explicitly described with more specifics about what the different slopes indicate. Figure 2 or S2 (how are they different?) aren't that helpful to your discussion. Yes all the slopes look pretty good - should we take away more than that?

Line 230: Including the k values you used here and whether they were corrected for the ambient temperature is important.

Line 235: Again which butane compound are you using for your OH calculation? Both? [This becomes apparent later but this is where I want to know the details]

Line 236: Often there are O₃ deficits in the smoke plume center due to the rapid chemistry happening creating strong gradients in O₃ concentration. How sensitive are your derived OH concentrations to the range of O₃ in a particular transect? I realize that

you say the uncertainty of O₃ variation is taken into account in the total plume-average OH uncertainty but on a component by component basis how much uncertainty is each term contributing? Also reference your table in the supplement here with the OH uncertainty and add the OH concentration to the table too so we can compare the uncertainty to the value.

Line 252: 27% higher is not slight but from the figure it does appear to be within the error of the calculation. Either say that or do a hypothesis test to show they aren't statistically different. Explain why there might be a systematic bias in the reaction rate at low temperature. Do you see a trend in the comparison with temperature? Is there a study you can cite to support the suspected bias in k ?

Line 305: I suggest showing the OH concentrations first (Fig 3) since they are used in Figure 1 for the blue curves. When they are first mentioned is when I want to know more about them.

Line 309: Does it really represent an upper limit on the emitted HCHO? That implies you know that there was no loss of HCHO in the plume prior to measurement. What evidence do you have to support this?

Line 313: What is the difference between the blue and the black curves? Blue: predicted decay of primary nHCHO from J and OH. Black: calculated primary nHCHO. These seem to be almost the same definition - or is there very little loss of the primary nHCHO. Perhaps refer to the equations to highlight which terms are different? The two lines are pretty similar for all shown cases - do both need to be shown? What is the main goal of showing both of these calculated trends? It would be better to show a figure related to the discussion of the fraction of primary v secondary HCHO over the lifetime of the plume (as discussed in the text) and how it varies. A figure like I just described would facilitate your analysis of the drivers of HCHO.

Line 322: This is not obvious in the figure since most start out with a positive trend in the measured values with time and then the loss overtakes the production. It just happens faster in the 3 you highlight with larger loss rates than production in the table. Perhaps you can color the fit line to show if the plume net loss exceeded production to make it clearer? It might be more informative to show the role of J and OH loss and the balance with production across the physical ages of the plume. A figure like this would more clearly show the point that I believe you are trying to make (what are the controls on HCHO concentration in fire plumes and how do they vary).

Section 3.2: This section needs to be the first part of the results and discussion section since the OH concentration is used to calculate the loss of primary nHCHO.

Section 3.3: At the beginning of this section remind the reader how you are determining secondary HCHO production - a mass balance approach with loss, production, and dilution terms - and not from VOC chemistry.

Line 360: Since secondary production was calculated with the OH concentrations I would expect there to be a correlation between the 2 terms. How does the correlation with J compare to that with OH? Or other oxidants? A more comprehensive analysis and discussion would guide the reader to the same conclusion that you make.

Line 366: A high R² doesn't necessarily mean that the relationship is significant. Including a statistical analysis with the p values with strengthen the conclusions you are making.

Line 368: What other potential drives of secondary HCHO production did you look at?

How does the trend/relationship change if the eastern US fire is excluded? It looks pretty different (high VOCs and nHCHO) and there is only one fire from that region.

Line 370: Why exclude NO₂ and CO in the OH reactivity analysis? If interested in the role of VOCs I understand but the controls on OH concentration will still include NO₂ and CO. I more complete analysis looking at both the total and VOC reactivity would improve the work since I expect there is variability in the NO₂ (and CO) that makes the VOC/total reactivity vary by plume.

Line 372: This sentence is a repeat of 368 and it still isn't clear if you actually are showing this.

Line 380: I don't understand this logic since it seems to contradict your analysis in the previous paragraph where you said a strong correlation indicated OH was an important driver. I can't really tell how different [OH-VOC reactivity/CO] is from [OH-VOC reactivity/CO * OH] but I imagine the values are scaled pretty linearly. It might be more informative [OH-VOC reactivity/CO] on the x-axis and getting rid of the colors in 4a since they are hard to see anyway. You could also show with [OH-VOC reactivity/CO * OH] to get the effective yield.

Line 401: What were the PTRMS measurements used for? It is unclear as written and how this information is related to the current discussion. Why is this one compound so important?

Line 407-11: You should not be comparing western and eastern fires give the number of eastern fires in this analysis is 1. You have no idea what if the fire was representative of other fires in the region. I suggest rewriting/adding that more data from eastern fires are needed to understand how they may be different as suggested by this one fire.

Line 436: Did you show that the variability in the reactive VOC pool is not playing an important role? I'm not sure the analysis presented before this does a good job of this since the figure is weighted by OH.

No technical comments.